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CLAIMS

[Claim(s)]

[Claim 1] Aliphatic polyester system biodegradable resin for shape-memory resin Plastic solid composition.

[Claim 2] A biodegradable shape-memory resin Plastic solid which comprised aliphatic polyester system biodegradable resin.

[Claim 3] At temperature of less than molding temperature, give modification to a Plastic solid which fabricated aliphatic polyester system biodegradable resin in predetermined shape which should be memorized at temperature more than the melting point of this resin, next was acquired, and it ranks second to it, A biodegradable shape-memory resin Plastic solid acquired by cooling to temperature of less than a glass transition point of this resin, and fixing deformed geometry.

[Claim 4] The directions for a shape-memory resin Plastic solid which specified shape of origin made to memorize by heating the Plastic solid according to claim 3 to a temperature higher than temperature which gave said less than molding temperature and modification is made to recover.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the shape-memory resin Plastic solid constituted the aliphatic polyester system biodegradable resin for shape-memory resin Plastic solid composition, and from now on. This invention relates also to the directions for said shape-memory resin Plastic solid.

[0002]

[Description of the Prior Art] The shape memory alloy is known as a material which has shape memory property. For example, there are a nickel titanium alloy, a copper-zinc-aluminum alloy, etc. and it is used for the thermal sensor of a toy, a pipe joint, and apparatus, etc. Although these shape memory alloys are excellent in shape memory property, they are dramatically expensive.

[0003] On the other hand, the shape-memory resin is also known as a material which has shape memory property. As for a shape-memory resin, it is possible to make it change at the temperature more than the glass transition point. It can cool to the temperature of less than a glass transition point, with deformed geometry maintained, deformed geometry can be fixed, and it has the character recovered in the original shape by heating the Plastic solid of this shape that changed to the temperature more than a glass transition point again.

[0004] As such a shape-memory resin, they are thermoplastics, such as poly norbornene (Nippon Zeon), a styrene butadiene copolymer (Asahi Chemical), and polyurethane (Mitsubishi Heavy Industries), and the transformer 1,4, for example. - Thermosetting resin, such as polyisoprene (Kuraray), is developed.

[0005] There is an advantage that these shape-memory resins are cheap compared with a shape memory alloy, it is lightweight, shaping is easy, and coloring can also be freed, and application development, such as a thermal sensor of medical supplies, a toy, teaching materials, a sport, autoparts, and apparatus, is furthered.

[0006]

[Problem(s) to be Solved by the Invention] However, although the conventional shape-memory resin is cheap compared with a shape memory alloy, it is still expensive and there is still a problem of the waste treatment after use. That is, like a general plastic, if incineration disposal of these resin is carried out, harmful gas will be emitted, land is also limited for laying

underground, and these processings pose a serious problem. When discarded in natural environment, it remains without decomposing for the stability of these resin, a scene is spoiled, and not only it but the problem of polluting the living environment of a marine organism is caused.

[0007]Then, the purpose of this invention solves the problem of the above-mentioned conventional technology, is cheaper than the conventional shape-memory resin, and there is in providing the shape-memory resin Plastic solid constituted the biodegradable resin for shape-memory resin Plastic solid composition in which the problem of the waste treatment after use is reduced, and from now on. The purpose of this invention is to provide the directions for said shape-memory resin Plastic solid.

[0008]

[Means for Solving the Problem]In order to solve the above problem, as a result of inquiring wholeheartedly, this invention persons find out that aliphatic polyester system biodegradable resin has shape memory property, and came to complete this invention.

[0009]That is, biodegradable resin of this invention is aliphatic polyester system biodegradable resin for shape-memory resin Plastic solid composition. A shape-memory resin Plastic solid of this invention comprises aliphatic polyester system biodegradable resin.

[0010]Hereafter, this invention is explained in detail. As aliphatic polyester system biodegradable resin in this invention, For example, poly, such as polyglycolic acid and polylactic acid (alpha-hydroxy acid); Poly, such as poly-beta-hydroxybutyric acid (beta-hydroxy alkanoate); Poly, such as a Polly epsilon-caprolactone (omega-hydroxy alkanoate); Polybutylene succinate, Polyalkylene alkanoate, such as polyethylene succinate, etc. are mentioned. Generally these aliphatic polyester system resin is the melting point of 60-200 **, 40-80 ** of glass transition points, and a with a weight average molecular weight of about ten to 300,000 thing.

[0011]It excels in the biodegradation characteristic, living body safety is high, and polylactic resin is [among these] preferred at a point that lactic acid which is moreover a decomposition product is absorbed in the living body, a point that a price is cheap, a transparent point, a point with sufficient coloring nature, etc. For example, the biodegradation characteristic of poly L lactic acid resin is a biodegradable test for 44 days in compost, to cellulose being 73% of resolvability, shows 93% of resolvability and is dramatically excellent. A price of poly L lactic acid resin is as cheap as about 1 of a price of said conventional shape-memory resin (poly norbornene, a styrene butadiene copolymer, polyurethane, transformer 1,4 - polyisoprene) / four to 1/2.

[0012]As for polylactic resin, in this invention, it is preferred that they are the melting point of 160-200 **, 45-75 ** of glass transition points, and the weight average molecular weight 150,000-250,000. When a glass transition point is in such a range, when giving modification, it is easy to use temperature more than a glass transition point, and it can cool to temperature of less than a glass transition point, with deformed geometry maintained, deformed geometry can be fixed, and deformed geometry can be maintained near a room temperature. There is few tangle of a polymer chain that weight average molecular weight is less than 100,000, and shape memory property is hard to be revealed. On the other hand, if weight average molecular weight exceeds 300,000, a moldability will worsen easily.

[0013]Polylactic resin is poly DL lactic acid which contains poly L lactic acid or D lactic acid as a constitutional unit. At most 40-mol% of a composition content of D lactic acid unit in the above-mentioned poly DL lactic acid is desirable. If D lactic acid unit exceeds 40-mol %, a molecular weight of poly DL lactic acid which polymerized will become remarkably low (10,000 or less). Desirable polylactic acid is poly DL lactic acid which contains poly L lactic acid or D lactic acid up to 20-mol % as a constitutional unit in this invention.

[0014]Polylactic resin may be the lactic acid system copolymer to which copolymerization of a lactic acid monomer or lactide, and other copolymerizable ingredients was carried out. As such other ingredients, dicarboxylic acid, polyhydric alcohol, hydroxycarboxylic acid, lactone, etc. with a functional group of two or more ester bond plasticities are mentioned.

[0015]As dicarboxylic acid, succinic acid, azelaic acid, sebacic acid, terephthalic acid, isophthalic acid, etc. are mentioned. Aromatic polyhydric alcohol, such as what carried out the addition reaction of the ethylene oxide to a bisphenol as polyhydric alcohol, Ethylene glycol, propylene glycol, butanediol, hexandiol, Octanediol, glycerin, sorbitan, trimethylolpropane, Ether glycols, such as aliphatic polyhydric alcohol, such as neopentyl glycol, a diethylene glycol, triethylene glycol, a polyethylene glycol, and a polypropylene glycol, etc. are mentioned. As hydroxycarboxylic acid, what is indicated to glycolic acid, hydroxybutylcarboxylic acid, and other JP,6-184417,A is mentioned. As lactone, glycolide, epsilon-caprolactone glycolide, epsilon-caprolactone, beta propiolactone, delta-butyrolactone, beta- or gamma-butyrolactone, PIBARO lactone, delta-valerolactone, etc. are mentioned.

[0016]Polylactic acid is conventionally compoundable by a publicly known method. Namely, JP,7-33861,A, JP,59-96123,A, 44 polymers debate proceedings, and 3198-3199 It is compoundable to a page by direct dehydration condensation from lactic acid like a statement, or ring opening polymerization of lactic acid cyclic dimer lactide.

[0017]When performing dehydration condensation directly, L-lactic acid, D-lactic acid, DL-lactic acid, or which lactic acid of these mixtures may be used. When performing ring opening polymerization, L-lactide, D-lactide, DL-lactide, ****- lactide, or which lactide of these mixtures may be used.

[0018]Composition of lactide, refining, and polymerization operation, for example A U.S. Pat. No. 4057537 item specification, It is variously indicated in articles, such as the open European patent application No. 261572 specification, Polymer Bulletin, 14,491-495 (1985) and Makromol Chem., 187, and 1611-1628 (1986).

[0019]Although a catalyst in particular used for this polymerization reaction is not limited, a catalyst which consists of metal or metallic compounds usually chosen from a group which consists of periodic table IA fellows, IVA fellows, IIB fellows, IVB fellows, and VA fellows can be used. As a thing belonging to IA fellows, for example Hydroxide of an alkaline metal. (For example, sodium hydroxide, a potassium hydrate, lithium hydroxide, etc.), a salt (for example, sodium lactate and sodium acetate.) of an alkaline metal and weak acid Sodium carbonate, octylic acid sodium, sodium stearate, Lactic acid potassium, potassium acetate, potassium carbonate, octylic acid potassium, etc. can mention alkoxides (for example, sodium methoxide, a potassium methoxide, a sodium ethoxide, potassium ethoxide, etc.) of an

alkaline metal, etc. As a thing belonging to IVA fellows, for example A catalyst of an organic tin series. Others and powder tin etc. which are (for example, lactic acid tin, tartaric acid tin, JIKAPURIRU acid tin, dilauryl acid tin, dipalmitate tin, distearic acid tin, Gio Reign acid tin, alpha-NAFUETO acid tin, beta-NAFUETO acid tin, octylic acid tin, etc.) can be mentioned. As a thing belonging to IIB fellows, zinc dust, zinc halide, a zinc oxide, an organic zinc system compound, etc. can be mentioned, for example. As a thing belonging to IVB fellows, zirconium system compounds, such as titanium system compounds, such as tetrapropyl titanate, and zirconium isopropoxide, etc. can be mentioned, for example. As a thing belonging to VA fellows, antimony system compounds, such as antimonous oxide, etc. can be mentioned, for example. Also in these, a catalyst which consists of tin or a tin compound is preferred especially from a point of activity. Generally the amount of these catalysts used is about 0.001 to 5 % of the weight to lactide.

[0020]Under existence of the above-mentioned catalyst, although a polymerization reaction changes with catalyst species, it can be performed at temperature which is usually 100 ** - 200 **. It is also preferred to perform a two-step polymerization like a statement to JP,7-247345,A.

[0021]In this invention, to aliphatic polyester system resin which has biodegradability. If needed Plasticizers (phthalic ester etc.), stabilizer (calcium stearate etc.), colorant (the shakkou chrome yellow, titanium oxide, etc.) and a bulking agent (calcium carbonate and clay.) Various, conventionally publicly known additive agents [, such as antioxidants (alkylphenol, organic phosphite, etc.), ultraviolet ray absorbents (salicylate, benzotriazol, etc.), fire retardant (phosphoric ester, antimony oxide, etc.) and a spray for preventing static electricity,], such as talc, can be blended. These loadings can be suitably defined according to the purpose of use.

[0022]A method in particular of blending the various above-mentioned additive agents with aliphatic polyester system resin which has biodegradability in this invention is not restricted, and can be conventionally performed by a publicly known method. For example, what is necessary is just to carry out a mix using a mill roll, a Banbury mixer, a super mixer, a monopodium, or a twin screw extruder.

[0023]Thus, a kneaded resin composition is fabricated in predetermined shape which should be memorized at temperature more than the melting point of this resin. This shaping can be performed like a general plastic with forming processes, such as extrusion molding, injection molding, vacuum forming, and compression molding, for example. Molding temperature is usually about 100-300 **.

[0024]Next, more than a glass transition point of this resin, modification is given to an acquired Plastic solid, it ranks second to it at temperature of less than molding temperature, and a shape-memory resin Plastic solid which changed can be acquired by cooling to temperature of less than a glass transition point of this resin, and fixing deformed geometry.

[0025]Modification is performed at temperature of less than said molding temperature more than a glass transition point of resin. Although a minimum of temperature which gives modification is usually the temperature more than a glass transition point, it is also possible to give modification at temperature of less than a glass transition point. On the other hand, a

maximum of temperature which gives modification is the temperature of less than said molding temperature. New shape will be given to a Plastic solid when modification is given at temperature more than molding temperature.

[0026]When changing, a Plastic solid can be placed under such a temperature atmosphere (for example, inside of heated air, warm water, and a steam), and it can carry out using suitable arbitrary means, for example, an empty hand, a suitable mold, a roll, a draft gear, and an collimator.

[0027]Thus, if a Plastic solid which was able to give modification is cooled to temperature of less than a glass transition point, with that deformed geometry maintained, a biodegradable shape-memory resin Plastic solid in which deformed geometry was fixed is acquired, and this deformed geometry can be maintained in near a room temperature.

[0028]Specified shape of origin made to memorize can be made to recover a resin-molding object of this deformed geometry by using temperature higher than temperature which gave modification with said less than molding temperature. Generally, time which shape recovery takes becomes short by using high temperature. shape recoverability in this case is equivalent to the conventional shape-memory resins (poly norbornene etc.) -- it excels. Thus, repeated use of the resin-molding object can be carried out by carrying out shape recovery.

[0029]Since a biodegradable shape-memory resin Plastic solid of this invention is excellent in shape recoverability, Medical supplies, such as the same use as the conventional shape-memory resin Plastic solid, for example, gypsum, and patching of pole, It can use for uses, such as gap material of a toy, teaching materials, sporting goods, autoparts, a thermal sensor of apparatus, a jointing material of a variant pipe, a lining material of a pipe inner surface or a laminate material, a pipe and an outside laminate material of a rod-like structure, a heat contraction nature tube, a bumper for cars, and a housing partition. Also in these, endurance is not needed so much, i.e., in medical supplies, such as a use which duration of service ends at an early stage, for example, gypsum, and patching of pole, a toy, teaching materials, sporting goods, and housing equipment, uses, such as a temporary target or various members which are used temporarily, are preferred. Since a biodegradable shape-memory resin Plastic solid of this invention is using biodegradable resin as a composition raw material and it has the biodegradation characteristic, discarding treatment after use is easy.

[0030]In this invention, polylactic acid system resin is preferred as aliphatic polyester system biodegradable resin, and poly L lactic acid resin is especially preferred.

[0031]

[Example]Hereafter, an example explains this invention still more concretely.

[0032]Synthetic example L lactide (made by Shimadzu) 100 weight section of [Example 1] poly L lactic acid, lauryl alcohol 0.05 weight section, and octylic acid tin (made in [Goldschmidt "cosmos 29"], catalyst for ring opening polymerization) 0.2 weight section were supplied to the feeding part of the 2 axis extruding kneading machine. 190 ** of cylinder temperatures and rotation supplied nitrogen gas from the feed hopper as 60 rpm of the directions. The mean residence time in a 2 axis extruding kneading machine was 15 minutes. The obtained polymer was extruded from the nozzle with a caliber of 2 mm. After carrying out cooling solidification of this, it cut

and the chip of poly L lactic acid resin was obtained. The obtained chip was a thing of the weight average molecular weight 180,000, the melting point of 178 **, and 68 ** of glass transition points.

[0033][Example 2] The above-mentioned poly L lactic acid resin was fabricated with the twin screw extruder, and thermofusion extrusion and a 0.4-mm-thick sheet were fabricated at 180 **. This sheet was cut in size of 50 mm x 30 mm. The obtained sheet was dipped in a 70 ** warm-water tank for 2 seconds. As shown in drawing 1, the sheet (1) picked out from the warm-water tank was twisted around the left-hand forefinger (2) from the venter of the finger, as the long side became in the length direction of a finger, and it fixed for 15 seconds. The temperature of the sheet became about 30-35 ** in these 15 seconds, and the Plastic solid in which deformed geometry was fixed was acquired. This Plastic solid was stopped on the finger with the adhesive bandage, and it was considered as patching of pole of the fractured part.

[0034][Example 3] When used the dryer, and heat to the Plastic solid of the above-mentioned deformed geometry for 2 minutes, it was made to change into it, and it removed from the finger, then it dipped in a 75 ** warm-water tank for 2 seconds, the original sheet shape was recovered.

[0035]

[Effect of the Invention]In this invention, as mentioned above, aliphatic polyester system biodegradable resin is excellent in shape memory property, and is cheaper than the conventional shape-memory resin, and the problem of the waste treatment after use is reduced.

Therefore, it is dramatically suitable as a composition raw material of a biodegradable shape-memory resin Plastic solid.

[0036]Polylactic acid system resin as aliphatic polyester system biodegradable resin is excellent in the biodegradation characteristic, and its living body safety is high, and it is especially dramatically useful at the point that lactic acid which is moreover a decomposition product is absorbed in the living body, a cheap point, a transparent point, a point with sufficient coloring nature, etc.

[0037]The biodegradable shape-memory resin Plastic solid which comprised aliphatic polyester system biodegradable resin is applicable to various kinds of uses which are excellent in shape memory property and require heat modification nature and shape recoverability, and the waste treatment after use is easy for it.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is a figure for [which gives modification to the biodegradable shape-memory resin Plastic solid of this invention] on the other hand explaining a law governing the application of laws.

[Description of Notations]

- (1) -- Sheet
- (2) -- Finger

[Translation done.]

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DRAWINGS

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